Berry-phase Modern Theory of Orbital Magnetization

Timo Thonhauser
thonhauser@wfu.edu
http://www.wfu.edu/~thonhat

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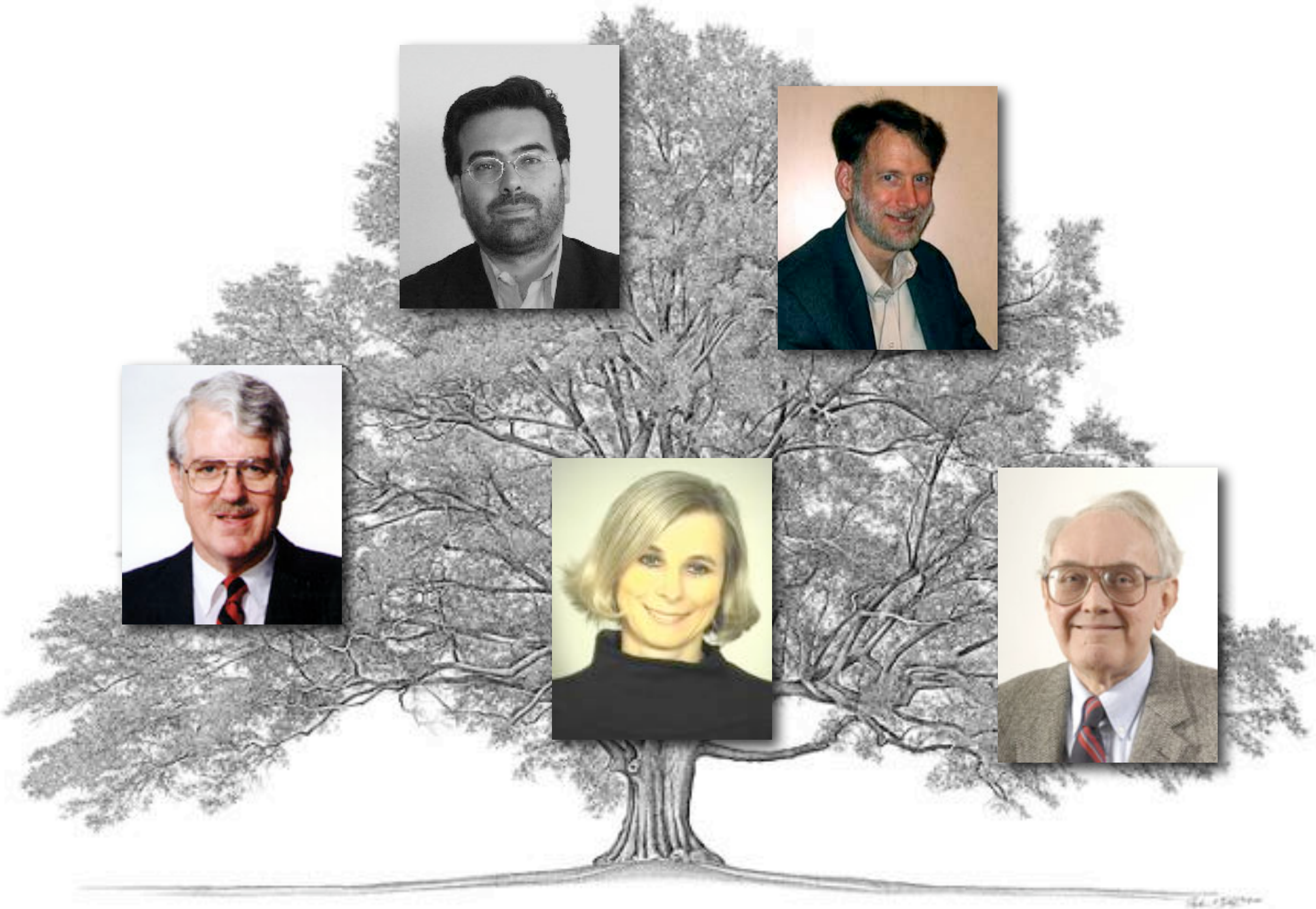


Get it now: Fully self-consistent implementation in PWscf!!!

vdW-DF: $$E_c^{\mathrm{nl}}[\rho] = \frac{1}{2}\int d^3r\, d^3r'\, \rho(\vec{r})\phi(\vec{r},\vec{r}')\rho(\vec{r}')$$

Langreth et al., Phys. Rev. Lett. 92, 246401 (2004).
Thonhauser et al., Phys. Rev. B 76, 125112 (2007).

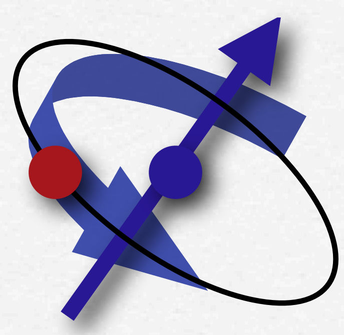
Outline

Orbital magnetization

First-principles theory of NMR

Magnetism ...

... in atoms



magnetic moment
from spin

+

magnetic moment
from orbital current

... in solids

$$\vec{H} = \vec{B} - 4\pi\vec{M}$$

$$\vec{M} = \vec{M}_{\text{spin}} + \vec{M}_{\text{orbital}}$$

No theory for periodic solids!

How can we calculate the orbital magnetization in periodic solids

?

Why not through current J?

- Microscopic $\vec{M}(\vec{r}):\quad \nabla\times\vec{M}(\vec{r})=\vec{J}(\vec{r})$
- Ill-defined: $\vec{M}(\vec{r})\Rightarrow\vec{M}(\vec{r})+\vec{M}_0+\nabla\eta$
- Therefore, cannot define $\vec{M}$ as cell average of $\vec{M}(\vec{r})$

M is not, even in principle, a functional of the bulk current density J(r). (Hirst, RMP 1997)

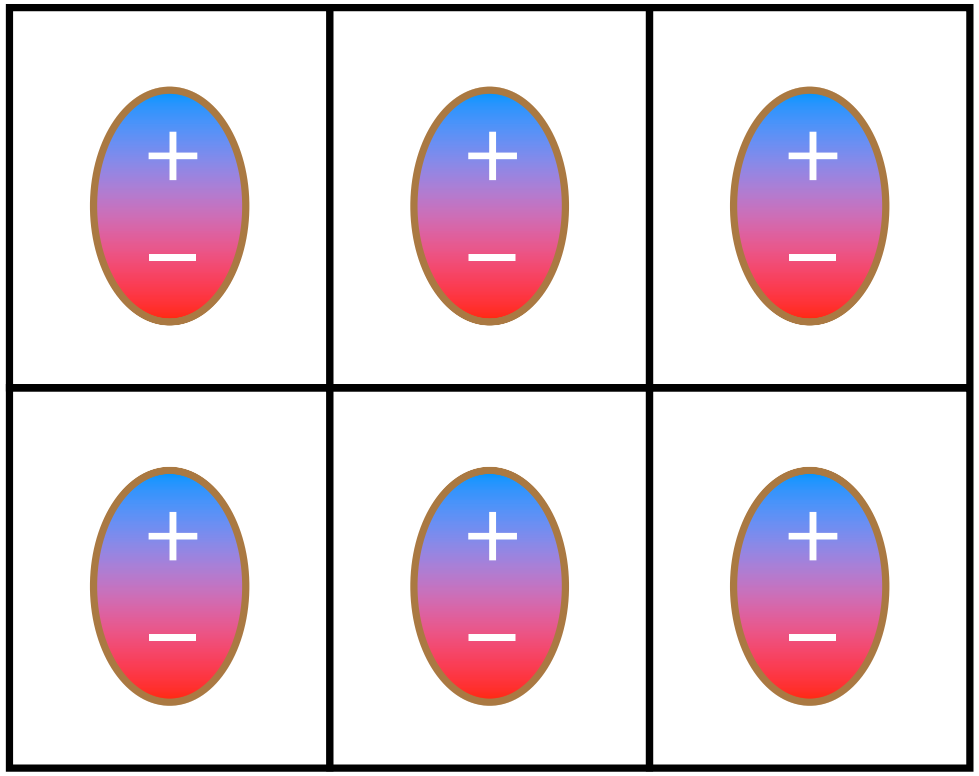
Just as:
P is not, even in principle, a functional of the bulk charge density ρ(r).

Why not through current J?

$$\vec{M} = \frac{\vec{m}}{V} = \frac{1}{2V}\int \vec{r}\times\vec{J}(\vec{r})\,dV$$

similar to polarization:

$$\vec{P} = \frac{\vec{d}}{V} = \frac{1}{V}\int \vec{r}\rho(\vec{r})\,dV$$



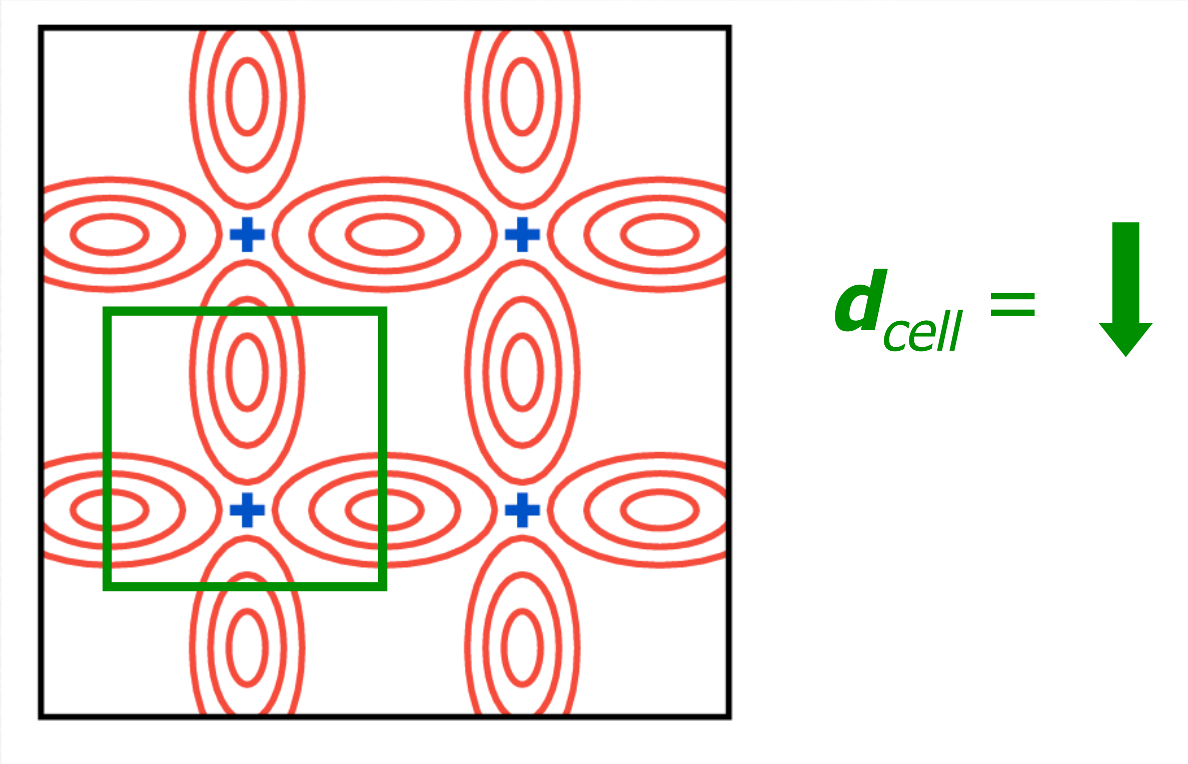
- Textbook picture (Claussius-Mossotti)
- But does not correspond to reality!

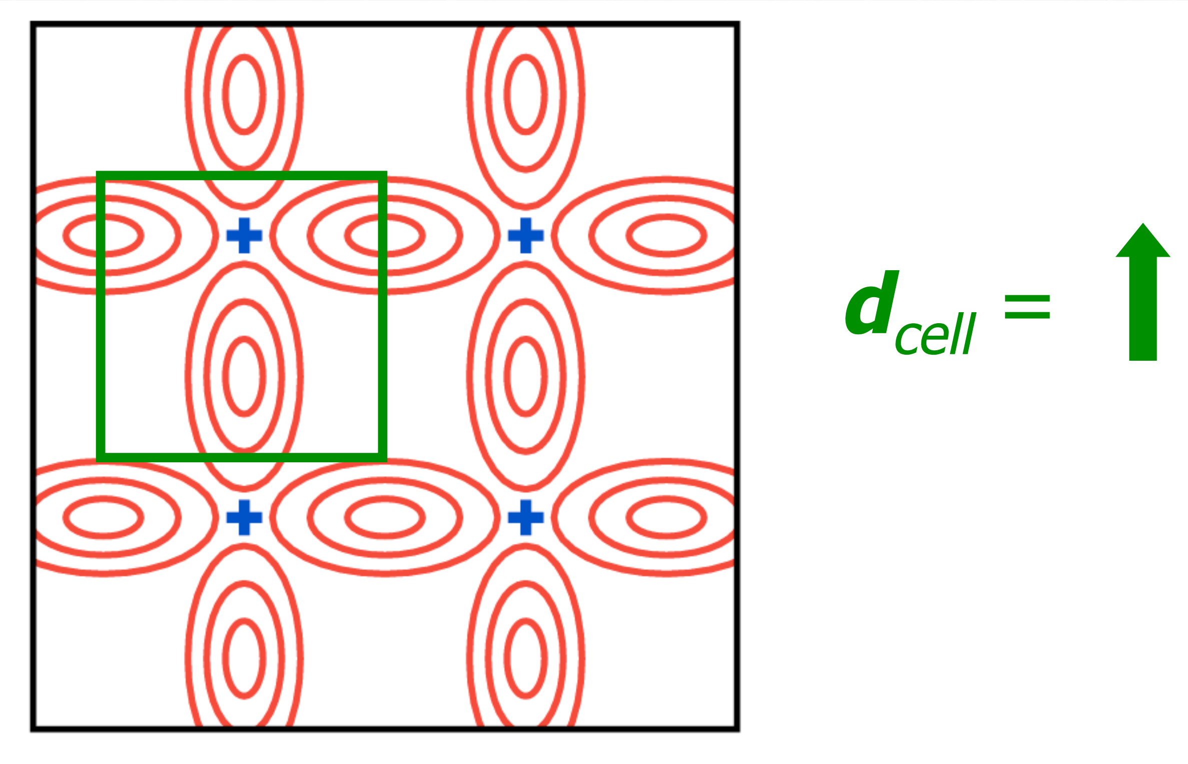
Why not through current J?

$$\vec{M} = \frac{\vec{m}}{V} = \frac{1}{2V}\int \vec{r} \times \vec{J}(\vec{r})\, dV$$

similar to polarization:

$$\vec{P} = \frac{\vec{d}}{V} = \frac{1}{V}\int \vec{r}\rho(\vec{r})\, dV$$





Vocabulary (one band in 2D)

Berry connection

$$A_\alpha(\vec{k}) = i\langle u_{\vec{k}}|\partial/\partial k_\alpha|u_{\vec{k}}\rangle$$

Berry curvature

$$\Omega(\vec{k}) = \nabla \times \vec{A}$$

Electric polarization

$$P_\alpha = \frac{q}{(2\pi)^2}\int_{BZ} A_\alpha(\vec{k})\, d^2k$$

Anomalous Hall conductivity

$$\sigma_{xy} = \frac{q^2}{(2\pi)^2\hbar}\int \Omega(\vec{k}) f(E_{\vec{k}} - \mu)\, d^2k$$

Chern number

$$C = \frac{1}{2\pi}\int_{BZ} \Omega(\vec{k})\, d^2k = \frac{1}{2\pi}\oint_{BZ} \vec{A}(\vec{k}) \cdot d\vec{k}$$

Terms & conditions

- ☐ one-particle H, broken TR
- ☐ B=0, or commensurate

1-particle states labeled by k

- ☐ ferromagnetic insulator
- ☐ zero Chern numbers

Wannier representable

- ☐ spinless electrons
- ☐ two dimensional
- ☐ isolated occupied band

for simplicity of presentation

- ☐ tight-binding model

for tests

Theory

Polarization

Magnetization

fi

$$\vec{d} = -e\sum_i \langle \psi_i | \vec{r} | \psi_i \rangle$$

eigenstates

$$= -e\sum_i \langle w_i | \vec{r} | w_i \rangle$$

loc. mol. orb.

thermod … imit

Theory

Polarization

Magnetization

finite samples

$$\vec{d} = -e \sum_i \langle \psi_i | \vec{r} | \psi_i \rangle$$
$$= -e \sum_i \langle w_i | \vec{r} | w_i \rangle$$

bulk Wannier functions |R>

therm

$$\vec{P} = \frac{\vec{d}}{A} = -\frac{e}{A_0} \langle \vec{0} | \vec{r} | \vec{0} \rangle$$

Theory

Polarization

...netization

circulation operator

finite samp...

$$\vec{d} = -e\sum_i \langle \psi_i|\vec{r}|\psi_i\rangle = -e\sum_i \langle w_i|\vec{r}|w_i\rangle$$

$$\vec{m} = -\frac{e}{2c}\sum_i \langle \psi_i|\vec{r}\times\vec{v}|\psi_i\rangle = -\frac{e}{2c}\sum_i \langle w_i|\vec{r}\times\vec{v}|w_i\rangle$$

thermodynamic limit

$$\vec{P} = \frac{\vec{d}}{A} = -\frac{e}{A_0}\langle\vec{0}|\vec{r}|\vec{0}\rangle$$

Theory

Polarization

Magnetization

finite samples

$$\vec{d} = -e \sum_i \langle \psi_i | \vec{r} | \psi_i \rangle = -e \sum_i \langle w_i | \vec{r} | w_i \rangle$$

$$\vec{m} = -\frac{e}{2c} \sum_i \langle \psi_i | \vec{r} \times \vec{v} | \psi_i \rangle = -\frac{e}{2c} \sum_i \langle w_i | \vec{r} \times \vec{v} | w_i \rangle$$

thermodynamic limit

$$\vec{P} = \frac{\vec{d}}{A} = -\frac{e}{A_0} \langle \vec{0} | \vec{r} | \vec{0} \rangle$$

$$\vec{M}_{\mathrm{LC}} = \frac{\vec{m}}{A} = -\frac{e}{2cA_0} \langle \vec{0} | \vec{r} \times \vec{v} | \vec{0} \rangle$$

Theory

Polarization

Magnetization

compare in a simple tight-binding model

$$\vec{m} = -\frac{e}{2c}\sum_i \langle \psi_i | \vec{r} \times \vec{v} | \psi_i \rangle$$
$$= -\frac{e}{2c}\sum_i \langle w_i | \vec{r} \times \vec{v} | w_i \rangle$$

$$\vec{M}_{\mathrm{LC}} = \frac{\vec{m}}{A} = -\frac{e}{2cA_0}\langle \vec{0} | \vec{r} \times \vec{v} | \vec{0} \rangle$$

A simple tight-binding model

VOLUME 61, NUMBER 18 PHYSICAL REVIEW LETTERS 31 OCTOBER 1988

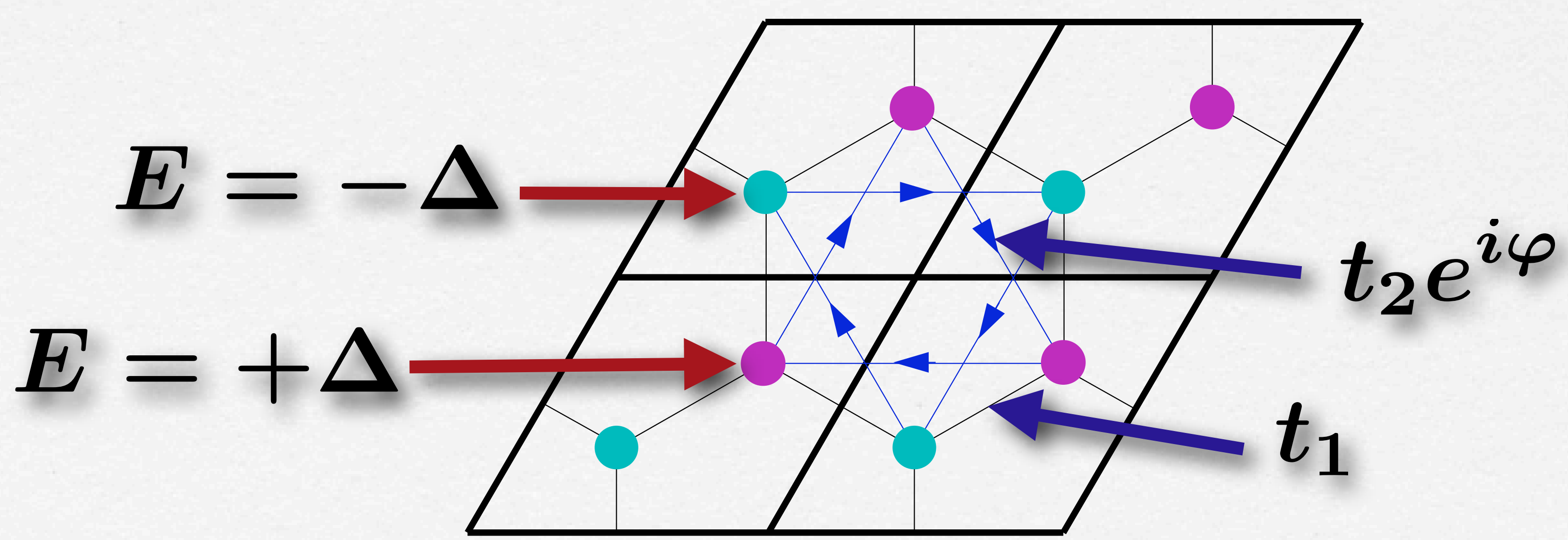
Model for a Quantum Hall Effect without Landau Levels: Condensed-Matter Realization of the "Parity Anomaly"

F. D. M. Haldane

Department of Physics, University of California, San Diego, La Jolla, California 92093

(Received 16 September 1987)

A two-dimensional condensed-matter lattice model is presented which exhibits a nonzero quantization of the Hall conductance σ^{xy} in the *absence* of an external magnetic field. Massless fermions *without spectral doubling* occur at critical values of the model parameters, and exhibit the so-called "parity anomaly" of (2+1)-dimensional field theories.



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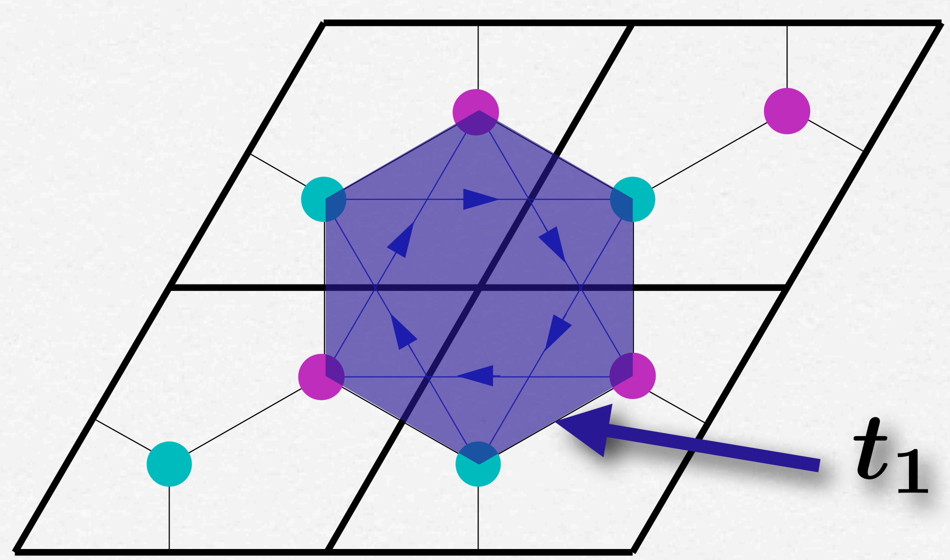
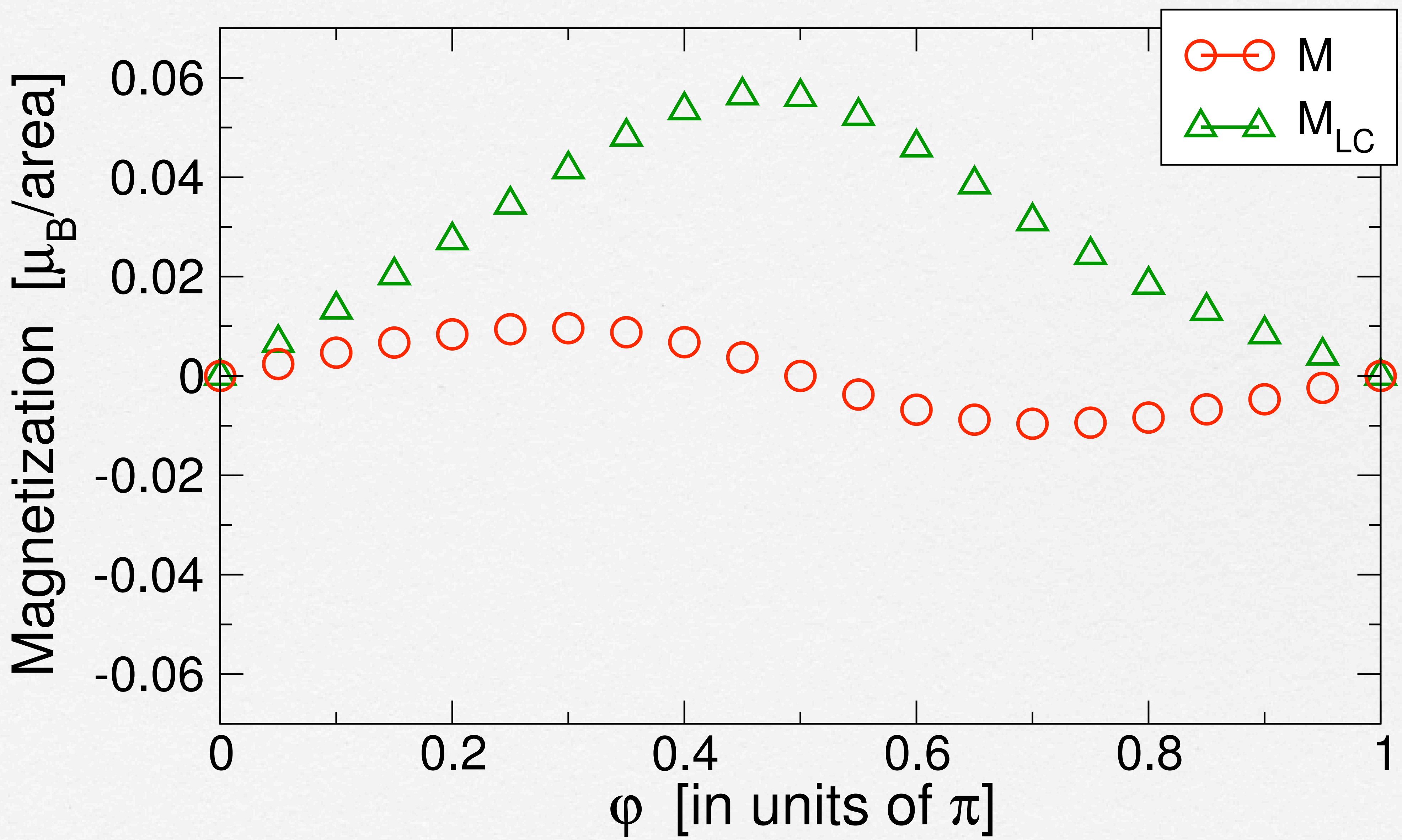


Compare - Numerical results



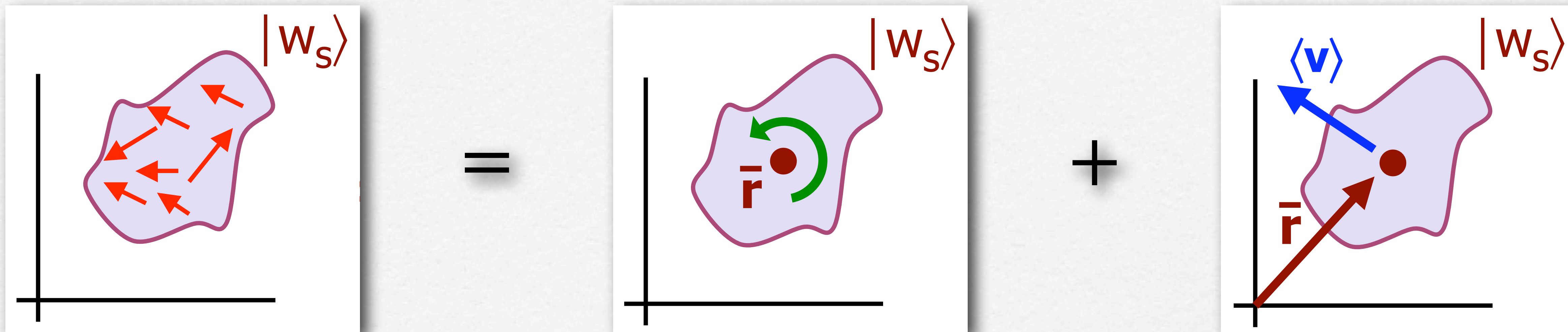
Something has gone wrong!

compare in a simple tight-binding model

$$\vec{m} = -\frac{e}{2c}\sum_i \langle \psi_i | \vec{r} \times \vec{v} | \psi_i \rangle$$
$$= -\frac{e}{2c}\sum_i \langle w_i | \vec{r} \times \vec{v} | w_i \rangle$$

$$\vec{M}_{\mathrm{LC}} = \frac{\vec{m}}{A} = -\frac{e}{2cA_0}\langle \vec{0} | \vec{r} \times \vec{v} | \vec{0} \rangle$$

Something has gone wrong!

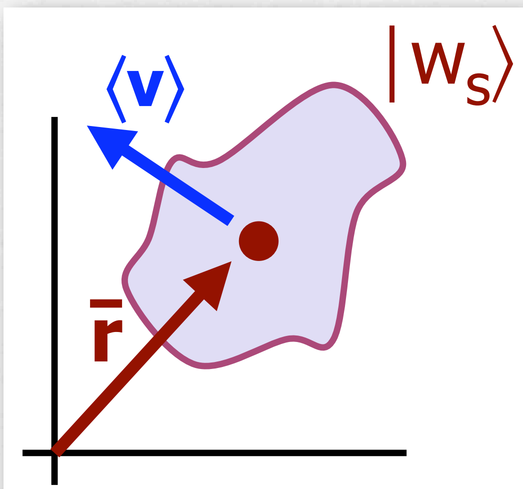


$$\langle w_s|\vec{r}\times\vec{v}|w_s\rangle = \langle w_s|(\vec{r}-\bar{r})\times\vec{v}|w_s\rangle + \bar{r}\times\langle w_s|\vec{v}|w_s\rangle$$

(LC) local circulation

(IC) itinerant circulation

Itinerant circulation



$$\bar{\boldsymbol{r}} \times \langle \boldsymbol{w_s} | \vec{\boldsymbol{v}} | \boldsymbol{w_s} \rangle$$

(IC) itinerant circulation

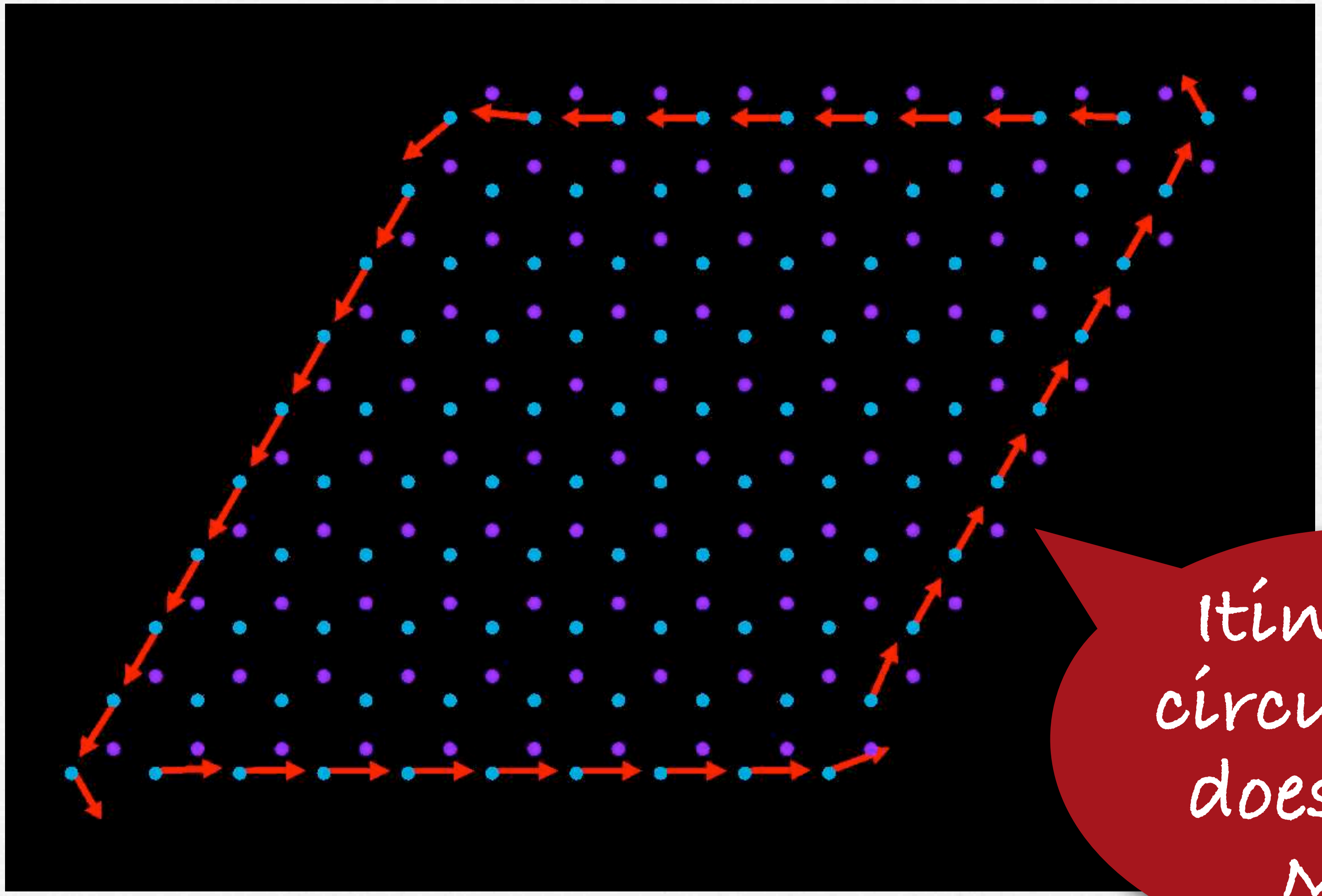
- bulk WF: bulk band carries no net current

  so <v>=0
  so r x <v>=0

- but what about surface WF?

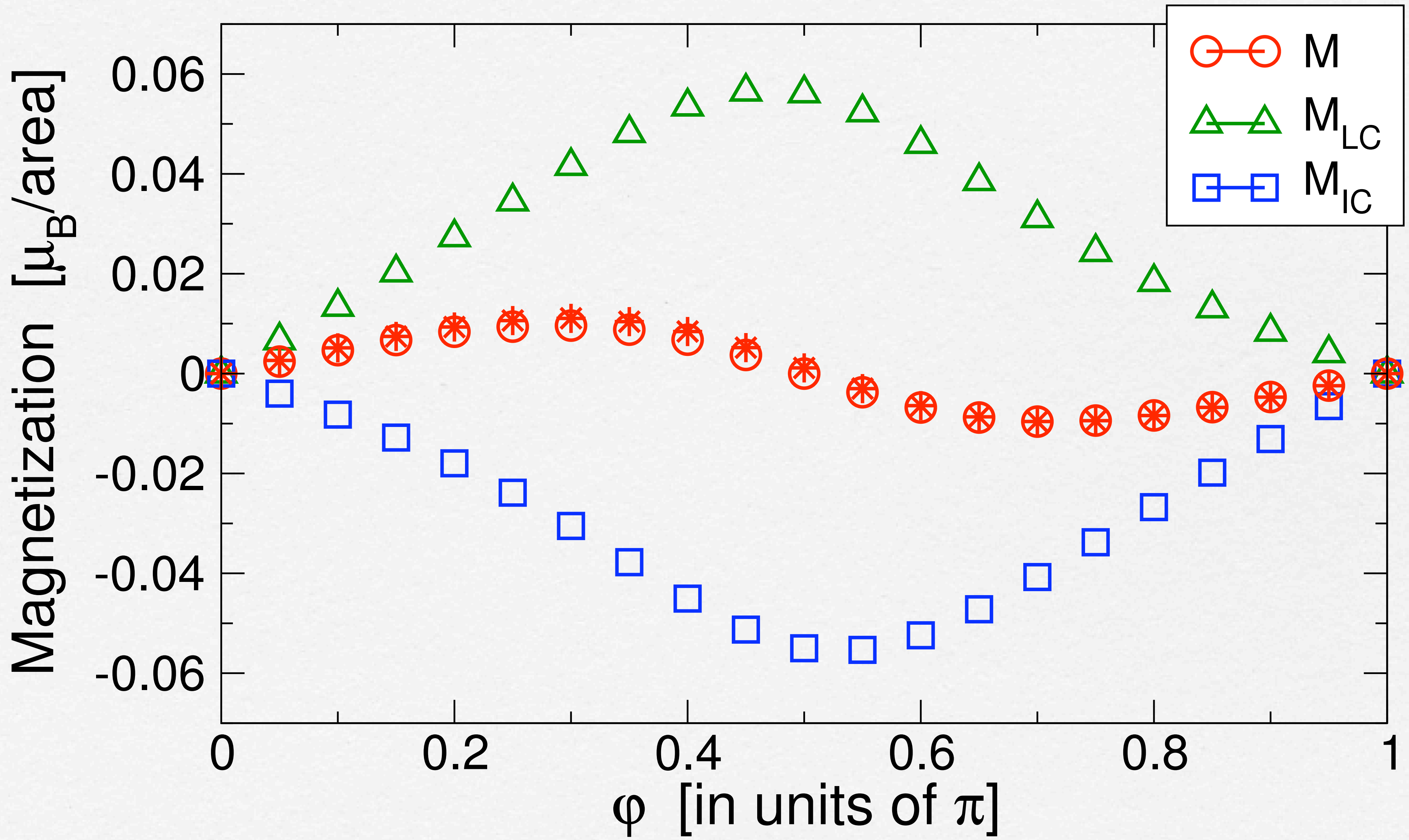
Itinerant circulation

WF currents $-e\langle w_i|\vec{v}|w_i\rangle$



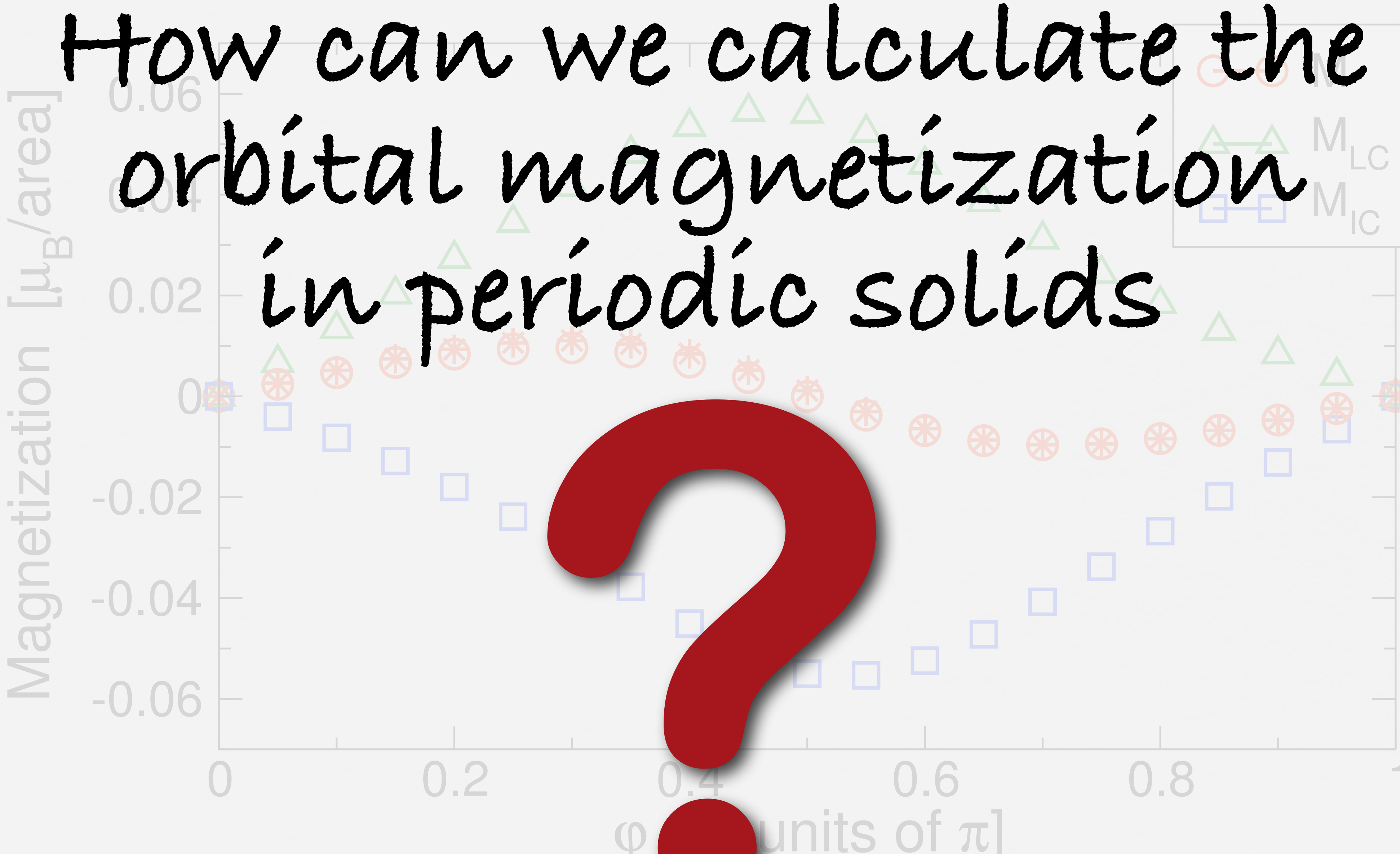
Itinerant circulation does exist M_{IC} !

Compare again!



Compare again!

How can we calculate the orbital magnetization in periodic solids



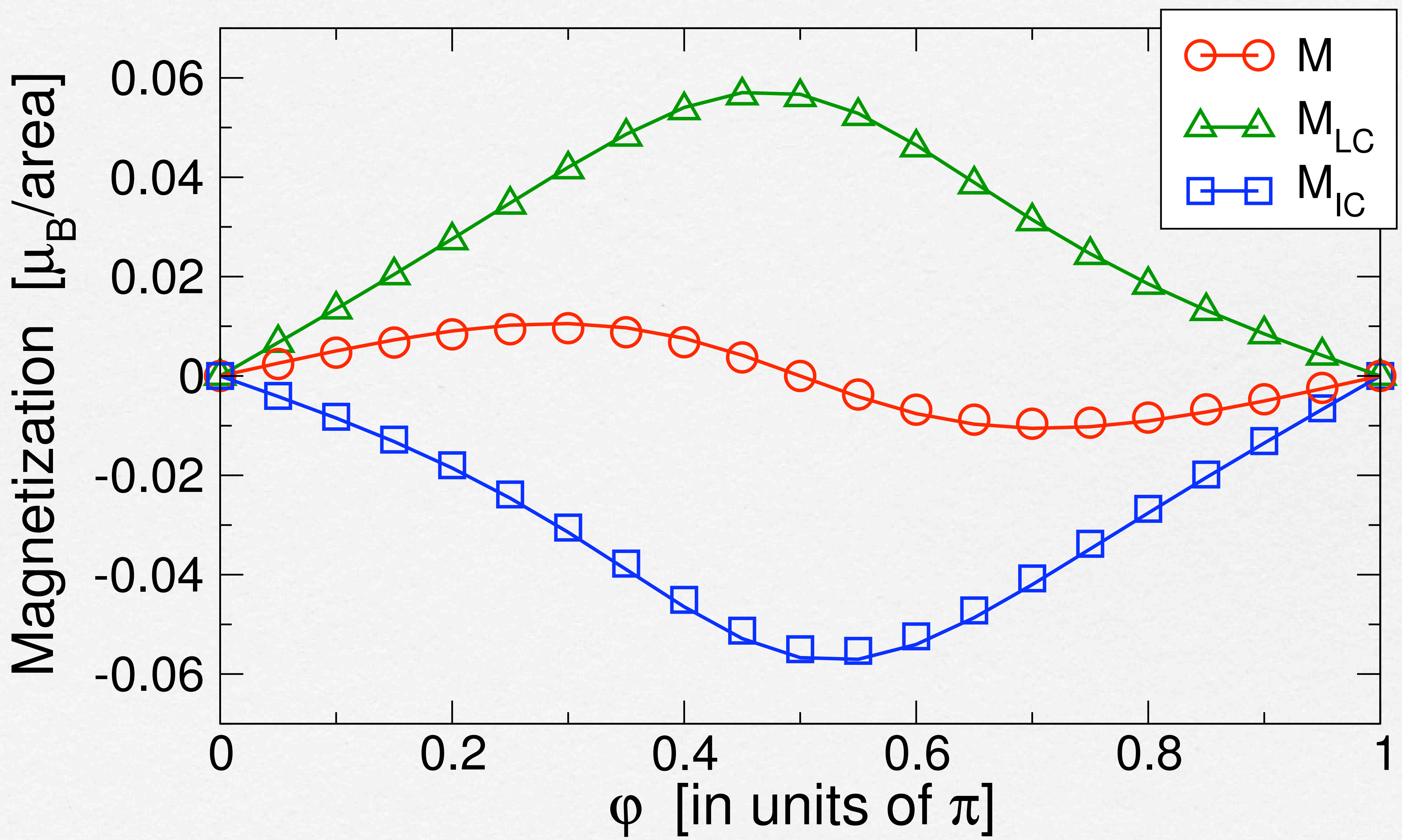
?

Final result

$$\vec{M} = \frac{e}{2\hbar c} \,\mathrm{Im} \int \frac{d^2k}{(2\pi)^2} \langle \partial_{\vec{k}} u_{\vec{k}} | \times (H_{\vec{k}} + E_{\vec{k}}) | \partial_{\vec{k}} u_{\vec{k}} \rangle$$

- Invariant under H → H+ΔE
- Gauge invariant $|u_{\vec{k}}\rangle \longrightarrow e^{i\phi(\vec{k})}|u_{\vec{k}}\rangle$
- Easy to discretize and implement

Perfect agreement!



Extensions

$$\vec{M} = \frac{e}{2\hbar c}\,\mathrm{Im}\sum_n \int_{\mathrm{BZ}} \frac{d^3k}{(2\pi)^3}\; f(E_{n,\vec{k}} - \mu)$$

$$\langle \partial_{\vec{k}} u_{n,\vec{k}} | \times (H_{\vec{k}} + E_{n,\vec{k}} - 2\mu) | \partial_{\vec{k}} u_{n,\vec{k}} \rangle$$

Extensions

$$\vec{M} = \frac{e}{2\hbar c} \mathrm{Im} \sum_n \int_{\mathrm{BZ}} \frac{d^3k}{(2\pi)^3} f(E_{n,\vec{k}} - \mu)$$

$$\langle \partial_{\vec{k}} u_{n,\vec{k}} | \times (H_{\vec{k}} + E_{n,\vec{k}} - 2\mu) | \partial_{\vec{k}} u_{n,\vec{k}} \rangle$$

- three dimensions

Extensions

$$\vec{M} = \frac{e}{2\hbar c}\,\mathrm{Im}\sum_{n}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\;f(E_{n,\vec{k}}-\mu)$$

$$\langle\partial_{\vec{k}}u_{n,\vec{k}}|\times(H_{\vec{k}}+E_{n,\vec{k}}-2\mu)|\partial_{\vec{k}}u_{n,\vec{k}}\rangle$$

- ☐ three dimensions
- ☐ multi-band

Extensions

$$\vec{M} = \frac{e}{2\hbar c} \operatorname{Im} \sum_n \int_{\mathrm{BZ}} \frac{d^3k}{(2\pi)^3} f(E_{n,\vec{k}} - \mu)$$

$$\langle \partial_{\vec{k}} u_{n,\vec{k}} | \times (H_{\vec{k}} + E_{n,\vec{k}} - 2\mu) | \partial_{\vec{k}} u_{n,\vec{k}} \rangle$$

- ☐ three dimensions
- ☐ multi-band
- ☐ metals ?
- ☐ Non-zero Chern No. ?

Papers

PRL **95,** 137205 (2005) PHYSICAL REVIEW LETTERS week ending 23 SEPTEMBER 2005

Orbital Magnetization in Periodic Insulators

T. Thonhauser,[1] Davide Ceresoli,[2] David Vanderbilt,[1] and R. Resta[3]

[1]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*
[2]*International School for Advanced Studies (SISSA/ISAS) and INFM-DEMOCRITOS, via Beirut 4, 34014, Trieste, Italy*
[3]*Dipartimento di Fisica Teorica Università di Trieste and INFM-DEMOCRITOS, strada Costiera 11, 34014, Trieste, Italy*

(Received 20 May 2005; published 22 September 2005)

Working in the Wannier representation, we derive an expression for the orbital magnetization of a periodic insulator. The magnetization is shown to be comprised of two contributions, an obvious one associated with the internal circulation of bulklike Wannier functions in the interior, and an unexpected one arising from net currents carried by Wannier functions near the surface. Each contribution can be expressed as a bulk property in terms of Bloch functions in a gauge-invariant way. Our expression is verified by comparing numerical tight-binding calculations for finite and periodic samples.

PRL 95, 137205 (2005)

Orbital magnetization in crystalline solids: Multi-band insulators, Chern insulators, and metals

Davide Ceresoli,[1] T. Thonhauser,[2] David Vanderbilt,[2] and R. Resta[3]

[1]*International School for Advanced Studies (SISSA/ISAS) and DEMOCRITOS, via Beirut 2-4, 34014 Trieste, Italy*
[2]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*
[3]*Dipartimento di Fisica Teorica Università di Trieste and DEMOCRITOS, strada Costiera 11, 34014 Trieste, Italy*

We derive a multi-band formulation of the orbital magnetization in a normal periodic insulator (i.e., one in which the Chern invariant, or in 2d the Chern number, vanishes). Following the approach used recently to develop the single-band formalism [T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. **95**, 137205 (2005)], we work in the Wannier representation and find that the magnetization is comprised of two contributions, an obvious one associated with the internal circulation of bulk-like Wannier functions in the interior and an unexpected one arising from net currents carried by Wannier functions near the surface. Unlike the single-band case, where each of these contributions is separately gauge-invariant, in the multi-band formulation only the *sum* of

PRB 74, 024408 (2006)

Papers

Metal	e	Expt. [22]	FLAPW [5]		This method	
			LDA	PBE	LDA	PBE
bcc-Fe	[001]	0.081	0.048	0.045	0.0640	0.0658
bcc-Fe	[111]	–	–	–	0.0633	0.0660
fcc-Co	[111]	0.120	0.076	0.073	0.0741	0.0756
fcc-Co	[001]	–	–	–	0.0642	0.0660
hcp-Co	[001]	0.133	–	–	0.0924	0.0957
hcp-Co	[100]	–	–	–	0.0837	0.0867
fcc-Ni	[111]	0.053	0.049	0.050	0.0545	0.0519
fcc-Ni	[001]	–	–	–	0.0533	0.0556

Ceresoli et al., arXiv: 0904.1988

Outline

Orbital magnetization → First-principles theory of NMR

How can we calculate ab-initio NMR spectra for periodic crystals in a simple way

?

Ab-initio NMR

NMR shielding tensor

F. Mauri, B. Pfrommer, and S. Louie, PRL 77, 5300 (1996).
D. Sebastiani and M. Parrinello, JCP 105, 1951 (2001).
C. J. Pickard and F. Mauri, PRB 63, 245101 (2001).

Ab-initio NMR

NMR shielding tensor

response to external field

Ab-initio NMR

NMR shielding tensor

~~response to external field~~

orbital magnetization

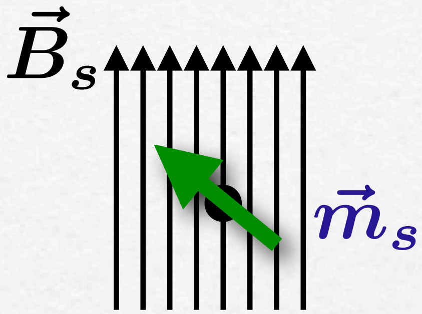
Ab-initio NMR

$$\vec{B}_{\boldsymbol{s}}^{\mathrm{ind}} = - \overleftrightarrow{\boldsymbol{\sigma}}_{\boldsymbol{s}} \cdot \vec{B}^{\mathrm{ext}}$$

$$\boldsymbol{\sigma}_{\boldsymbol{s},\boldsymbol{\alpha\beta}} = -\frac{\partial B_{\boldsymbol{s},\boldsymbol{\alpha}}^{\mathrm{ind}}}{\partial B_{\boldsymbol{\beta}}^{\mathrm{ext}}}$$

NMR and Orbital Magnetization

$$B_{s,\alpha} = B^{\text{ext}}_{\alpha} + B^{\text{ind}}_{s,\alpha}$$



$$E = -\vec{m}_s \cdot \vec{B}_s$$

$$\delta_{\alpha\beta} - \sigma_{s,\alpha\beta} = \partial B_{s,\alpha} / \partial B^{\text{ext}}_{\beta}$$

$$B_{s,\alpha} = -\partial E / \partial m_{s,\alpha}$$

NMR and Orbital Magnetization

$$B_{s,\alpha} = B_{\alpha}^{\text{ext}} + B_{s,\alpha}^{\text{ind}}$$

$$\delta_{\alpha\beta} - \sigma_{s,\alpha\beta} = -\frac{\partial}{\partial B_{\beta}} \frac{\partial E}{\partial m_{s,\alpha}} = -\frac{\partial}{\partial m_{s,\alpha}} \frac{\partial E}{\partial B_{\beta}}$$

$$= \Omega \frac{\partial M_{\beta}}{\partial m_{s,\alpha}}$$

$$\vec{B}^{\text{ext}} = 0$$

Reminder: Born eff. Charges

$$Z^*_{\alpha\beta}$$

force F_s in direction α on site r_s by E in direction β

β component of P induced by displacement of s in direction α

$\vec{E} = 0$

$$Z^*_{s,\alpha\beta} = -\frac{\partial}{\partial \mathcal{E}_\beta}\frac{\partial E}{\partial r_{s,\alpha}} = -\frac{\partial}{\partial r_{s,\alpha}}\frac{\partial E}{\partial \mathcal{E}_\beta} = \Omega\frac{\partial P_\beta}{\partial r_{s,\alpha}}$$

In Practice ...

$$\sigma_{s,\alpha\beta} = \delta_{\alpha\beta} - \Omega \frac{\partial M_\beta}{\partial m_{s,\alpha}} \approx \delta_{\alpha\beta} - \Omega \frac{\Delta M_\beta}{\Delta m_{s,\alpha}}$$

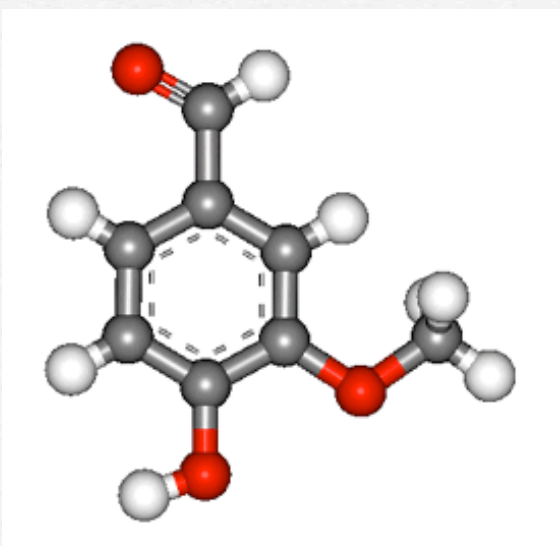
$$H = \left(\vec{p} + \frac{e}{c}\vec{A}(\vec{r})\right)^2 + V(\vec{r})$$

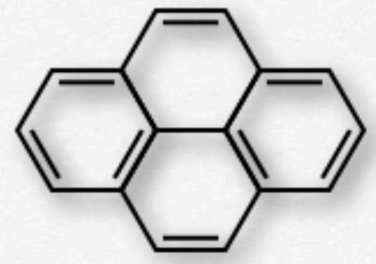
$$\tilde{\vec{A}}(\vec{G}) = -\frac{4\pi i}{\Omega}\frac{\vec{m}_s \times \vec{G}}{G^2}\,\mathrm{e}^{-i\vec{G}\cdot\vec{r}_s}$$

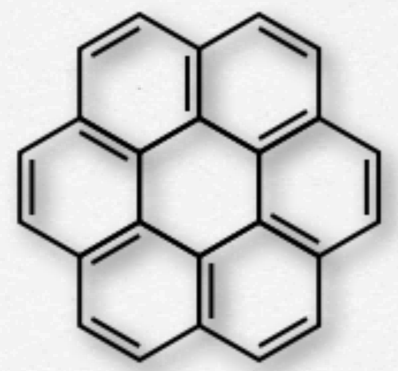
transverse gauge $\nabla \cdot \vec{A} = 0$

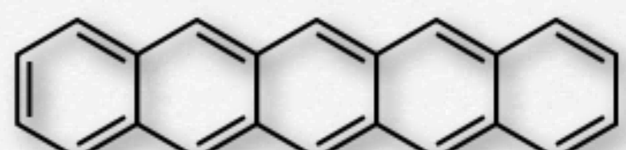
How well does it work?

molecules

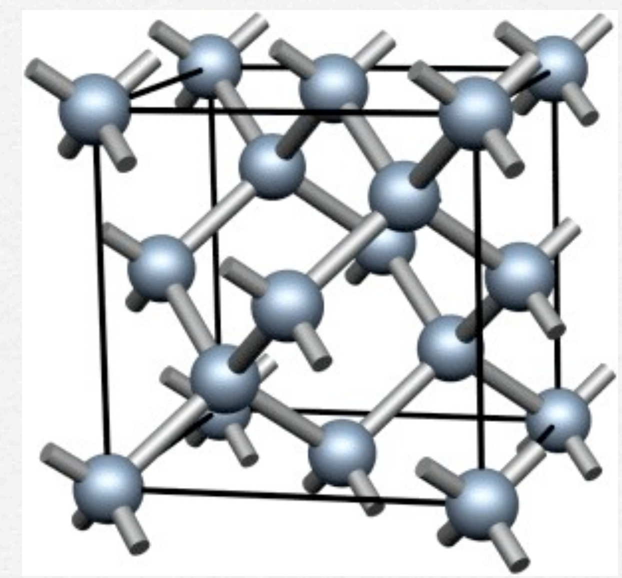








solids

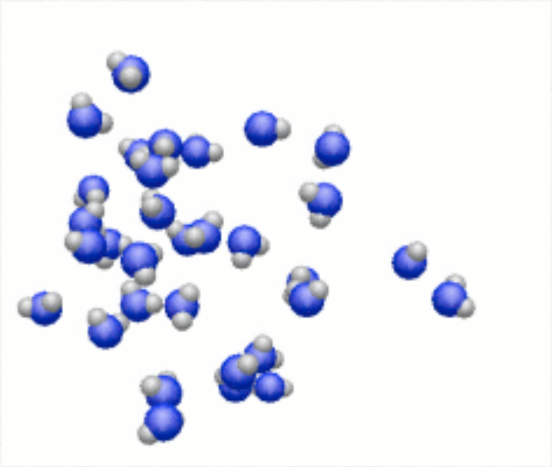


T. Thonhauser et al., J. Chem. Phys. 131, 101101 (2009).

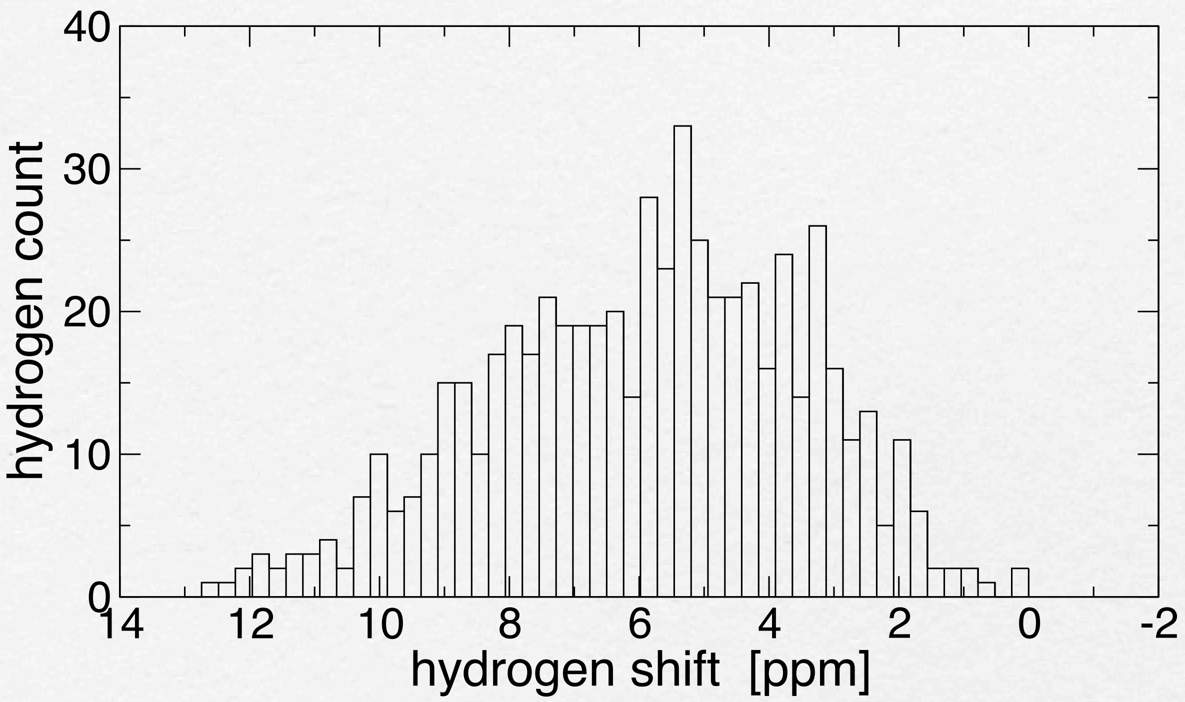
Outline

Orbital magnetization → First-principles theory of NMR

NMR of bulk water



64 water molecule unitcell (192 atoms)



Average
current work: 5.94 ppm
experiment: 5.84 ppm

SD
current work: 2.4 ppm
experiment: 2.4 ppm

Acknowledgments

Davide Ceresoli

David Vanderbilt

Nicola Marzari

Raffaele Resta

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UNIVERSITY